X−ray Absorption Spectroscopy of Ge−Nanocluster Films

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INTRODUCTION

Clusters and nanocrystals show a wide variety of novel electronic, magnetic and catalytic prop−erties. Germanium clusters are of particular interest, as recent publications suggest, since they display a strong blue luminescence. However, it is not clear, if this is due to surface species, ox−ide layers or quantum confinement. The presented experiment focuses on X−ray absorption of Ge−clusters, which have been synthesized in a narrow size distribution, to unambiguously iden−tify quantum confinement effects in these nanostructures.

EXPERIMENT AND DISCUSSION

Clusters were formed by condensation of Ge−vapor in an Argon atmosphere *in situ* at beamline 8.0. The vapor was cooled by Argon gas and clusters condensed out of the oversaturated vapor and were deposited on a hydrogen passivated Si−substrate located one inch above the Ge−evaporator. The cluster size could be adjusted by two parameters, the crucible temperature and the Ar−pressure. Rising either of them forced larger clusters to form. The mass flow onto the substrate was controlled with a shutter which was opened only briefly. Typically the shutter was opened fifteen times for five seconds at Ar−pressures between 120 and 200mTorr.
The cluster sizes and geometries were characterized with an atomic force microscope (AFM). For that purpose, witness depositions of clusters on highly orientated pyrolitic graphite (HOPG) were made. The lateral resolution of an AFM is limited by the diameter of the AFM tip, which is large compared to the clusters. For this reason it was assumed that the clusters are spherical in shape and the cluster height over the baseline was taken as the cluster size. It is interesting to note, that the clusters on HOPG are very mobile and hence, they gather at defects and step edges and form snowflake−like structures (Fig. 1). The sizes of the clusters produced in this experi−ment range from 2nm to 4nm, scaling almost linearly with the pressure of the Ar−atmosphere.
The conduction band of bulk Ge, Ge−clusters and GeO_2 powder was probed with total electron yield (TEY) X−ray absorption spectroscopy (XAS) at Beamline 8.0 at the Advanced Light Source. In this process a Ge 2p core electron was excited into the empty states of the conduction band. The spectra of bulk−Ge and GeO_2 show completely different features at the 2p edge (Fig. 2). Bulk−Ge has a very sharp absorption onset at around 1209eV and shows a weak excitonic feature right at the absorption edge (a) as well as some DOS features (b to d) [1,2]. The absorption onset of GeO_2 is shifted by about 5eV to higher energies and there is a strong excitonic fea−ture below the edge.
For Ge−clusters a blueshift of the absorption edge compared to the bulk is observed (Fig. 3). The shift gets larger for lower aggrega−

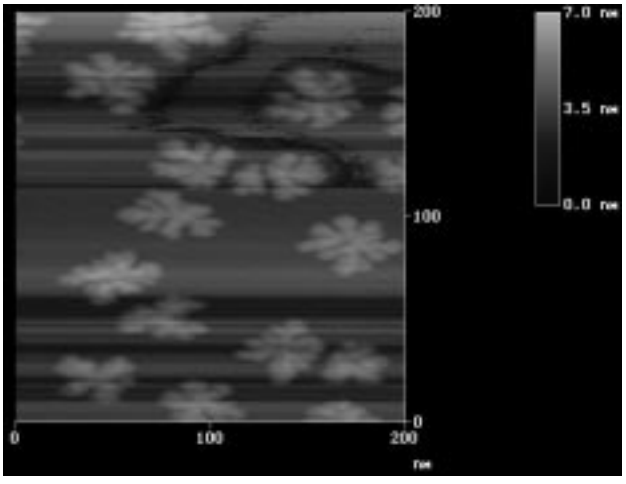

Fig. 1: Atomic Force Microscope image of Ge clusters on HOPG. Clusters gather at defects and step edges and form snowflake like structures.

tion pressures and smaller cluster sizes, respectively. The shift is measured at the intersection of the extrapolation of the edge to the background (Fig. 3) it ranges from 0.2eV for clusters of 3.5nm in size up to 0.4eV for clusters of 2.5nm in size. If it is measured at the inflection point of the edge it is even larger. The blueshift cannot be due to chemical shifts from oxidization as the characteristic absorption features of GeO_2 are missing i.e. the edge is similar in shape to the bulk absorption edge and the shift scales with the cluster size. However, the shift can be explained with quantum confinement effects in the cluster, which raise the bottom of the CB to higher energies depending on its size. In XAS the energy difference between the Ge 2p core level and the bottom of the conduction band is measured, hence a shift of the absorption edge implies, that the bottom of the conduction band is risen. As mentioned above, the cluster samples are made out of a size distribution of clusters and hence there will be a distribution of quantum shifts. Consequently, the absorption edges of the cluster samples are broadened compared to bulk-Ge.

SUMMARY

We were able to produce and deposit Ge clusters in the nm-range and for the first time a blueshift in the X-ray absorption from these clusters has been measured. The shift of the conduction band scales with the particle size, in agreement with quantum confinement theory.

ACKNOWLEDGMENTS

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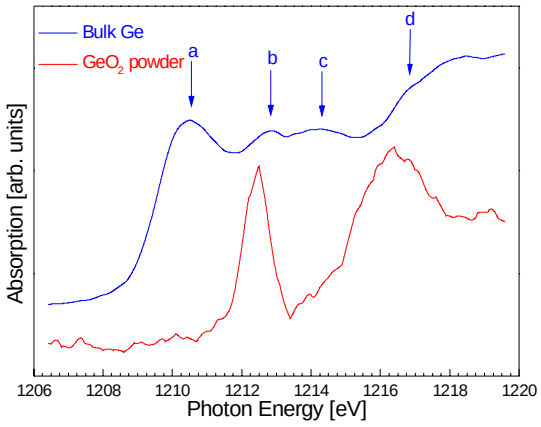

Fig. 2: Absorption spectra of bulk-Ge and GeO_2. In bulk-Ge an excitonic feature (a) as well as different DOS features can be seen (b-d) [1, 2]. The absorption onset of GeO_2 is moved to higher energies and there is a strong exciton below the edge.

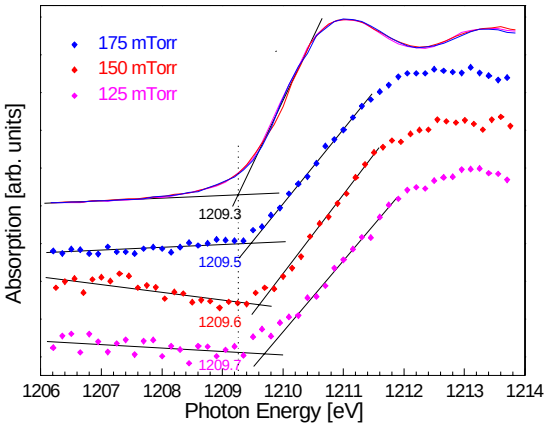

Fig. 3: X-ray absorption of bulk-Ge (top) and Ge-clusters. With decreasing aggregation pressure and decreasing particle size, respectivly the absorption edge moves to higher energies.

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